A DISTRIBUTED GAS BREATHER FOR MICRO DIRECT METHANOL FUEL CELL (μ-DMFC)

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ABSTRACT

This paper introduces a distributed gas breather to remove the gas byproduct (CO_2) from the micro direct methanol fuel cell (μDMFC). The concept and device configuration of "distributed breathing" aim to improve the performance of the μDMFC by (1) decreasing flow resistance, (2) increasing the active electrode area, and (3) reducing or possibly eliminating the discrete gas separator. Experimental verification is provided by a prototype breather with microscale hydrophobic breathing holes, which successfully removed CO_2 bubbles from a mixture of weak sulfuric acid and sodium bicarbonate aqueous solution. The techniques to fabricate sub-micron hydrophobic breathing holes with good stability, which would enable integration of the breather into the eventual μDMFC system, are discussed.

INTRODUCTION

Recently, fuel cells have attracted considerable attention as a micro power source because of its potential for high energy capacity (several folds higher than lithium-based thin film batteries), with the μDMFC [1] [2] (Fig.1) leading the way.

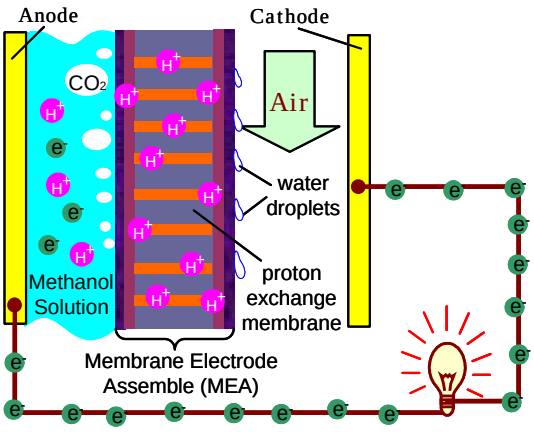

Fig. 1 Direct methanol fuel cell (DMFC)

However, development of the μDMFC faces new challenges not associated with its macroscale counterpart. The gas byproduct (CO_2 gas bubbles) generated in the fuel chamber (anode side) is one of such problems. In the regular (i.e. macroscale) DMFC, the fuel-gas mixture can flow through the anode side, where the gas is generated, along with the fuel stream, and get collected in a separator before the gas is released. In the micro channel of μDMFC, however, if not released efficiently, these bubbles can impede the fuel flow, decrease the effective reaction area, and cause excessive pressure buildup within the chamber, which lowers the efficiency and decreases the power output capability of μDMFC. These gas bubbles may even block the flow of fuel, as their sizes are comparable to the sizes of the microchannels in the μDMFC. An ideal solution for this problem is to breathe out these bubbles locally, or where they are generated, instead of consuming extra energy to push them all the way into a separated breather. A precursor of the desired distributed breather is the non-distributed degasser introduced in some biomedical applications [3]. However, higher degassing efficiency, more reliable leakage prevention, and adaptability into the anodic fuel chamber are required for a successful breather for the μDMFC.

BREATHING MECHANISM

We propose a new breathing strategy suitable for the μDMFC, characterized by "distributed breathing" throughout the anodic flow path designed to prevent the aggregation of minute gas bubbles into large ones. By keeping the growth of gas bubbles under check, performance of the μDMFC can be greatly improved by: (1) decreasing flow resistance, (2) increasing the active electrode area, and (3) reducing or eliminating the discrete gas separator.

Two features are essential in designing such a breathing scheme. First, gas bubbles should preferentially attach to the breathing spot, so that breathing holes need not be placed over the entire area of channel surface. Excessive exposure of the fuel to the air through the holes would lead to the loss of fuel by evaporation as well as diffusion of oxygen into the fuel. Second, the breathing holes should pass the gas, but should not allow fuel leakage.

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The breathing mechanism that fulfills these two features is explained in Fig. 2. Most of the inner surface of the channel is hydrophilic, which, incidentally, is necessary for effective fuel flow with minimum flow drag. Only the breathing holes and their immediate vicinity are made to be hydrophobic, allowing these areas to be landing sites for gas bubbles. The inner walls of the breathing holes in Fig. 2 also need to be made hydrophobic to prevent the leakage of liquid under fluctuation and accidental buildup of pressure.

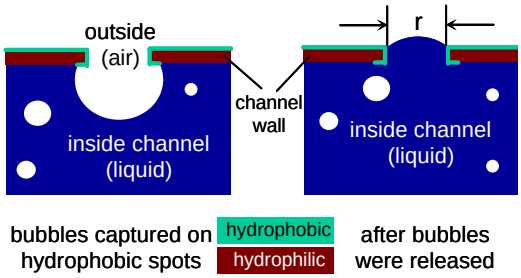

Fig. 2 Breathing mechanism (the concept)

The bubble-capturing phenomenon is opposite (but similar in concept) to the usual droplet-capturing by hydrophilic spots on a hydrophobic surface (e.g., [4]). In the experiment shown in Fig. 3, we prepared a hydrophilic sample (oxidized silicon wafer) that has hydrophobic spots (HMDS-coated) in a square-grid pattern and immersed the sample into 5% H_2SO_4. When hydrogen gas bubbles are generated by electrolysis and brought to the sample's surface by buoyancy, the gas bubbles preferentially attached onto the hydrophobic spots.

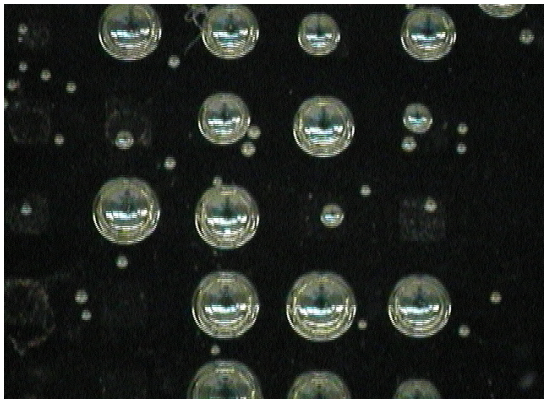

Fig. 3 Gas bubbles captured on
a grid of hydrophobic square spots

This preliminary experiment confirms that gas bubbles in a liquid flow can indeed be captured by hydrophobic patterns on a hydrophilic surface, which means that the bubbles in a flow should show a tendency to attach onto hydrophobic spots instead of other field areas that are hydrophilic.

FABRICATION OF BREATHING TEST CHIP

The process flow of the breathing sample is shown in Fig. 4. A (100) silicon wafer were firstly thinned down to about 150μm at specific locations by KOH. Clear breathing holes (50μm in diameter) were etched in the thinned sections by subsequent through-wafer etching by DRIE. A ~0.1μm SiO_2 layer was grown on the sample surface by oxidation to make it hydrophilic. The sample was then immersed into 0.2% Teflon® solution to coat a hydrophobic layer onto its surface and then blow dried by a strong nitrogen flow vertical to the surface, immediately after it was taken out of the Teflon® solution so as to keep the breathing holes from being blocked. The hydrophobic layer was patterned by oxygen RIE at 200mTorr and 200W for 5min with a 1.6μm AZ5214 PR mask. The finished chip was then packaged into an experiment setup for breathing test.

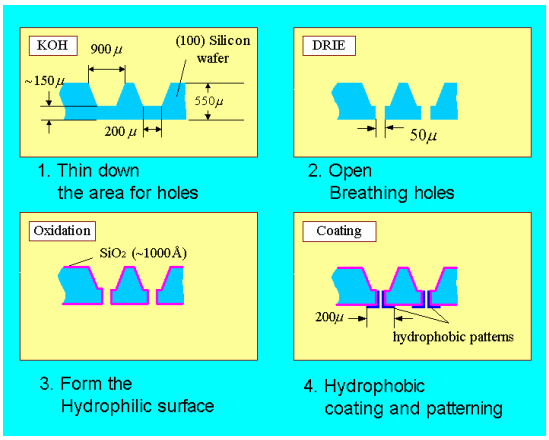

Fig. 4 Process flow to
fabricate the breathing test chip

EXPERIMENS AND RESULTS

The breathing experiment setup is shown in Fig. 5. A closed channel was formed by positioning a breathing test chip on the top, a transparent slide at the bottom, and a spacer (about 1.5mm thick) between them. To emulate distributed CO_2 generation in a fuel cell, sodium bicarbonate solution and weak sulfuric acid were pushed into the channel by two individual syringes sequentially. Bubble generation is more distributed in this method, compared with electrolysis. Under proper conditions, CO_2 gas bubbles could then be breathed out through the vertical breathing holes.

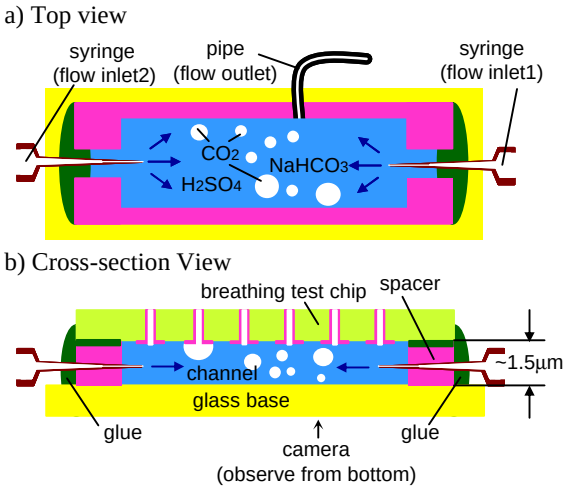

Fig. 5 Breathing experiment setup

The breathing process was recorded by a CCD camera, as shown in Fig. 6: Chemical-reaction-induced gas bubbles grew and reached the maximum at about 27s. After that, the bubbles were shown to be reduced by breathing out through the breathing holes, shrinking to very small ones, and eventually leaving most of the surface area free of bubbles. An identical experiment with no breathing holes showed no reduction of bubbles, eventually leading to bubbles covering almost the entire surface.

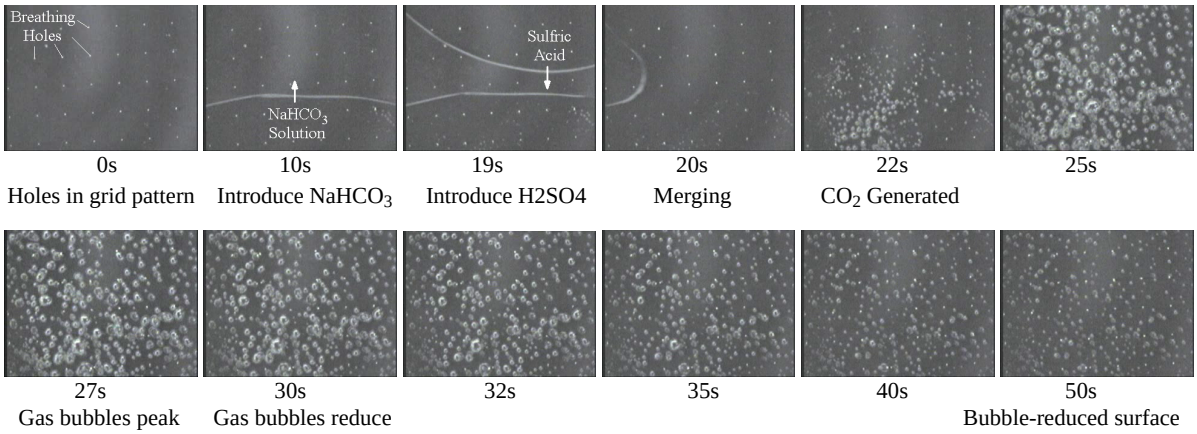

Fig. 6 Video clips of breathing process

DISCUSSIONS

Hydrophobic coating techniques

The properties of the hydrophobic layer are critical in the breathing process. First, the hydrophobicity should be as high as possible to capture gas bubbles efficiently and prevent liquid leakage. Second, the coating needs to be stable enough to work reliably inside the actual µDMFC system.

So far, four techniques have been tested to coat and pattern hydrophobic layer, as listed and compared in Table 1,. HMDS coating is the simplest and most convenient way for preliminary investigation. However, it may not be robust enough for long-term usage in the actual fuel cell systems. Teflon® provides the highest hydrophobicity and exhibits excellent stability for long-term application. But current liquid-phase coating method of Teflon® tends to block the breathing holes during deposition, especially for smaller breathing holes, which are desired for fuel leakage prevention, as discussed further below. Coating method with better conformity is necessary to make Teflon® deposition suitable for smaller (i.e. submicron) hydrophobic breathing holes. Better step-coverage and uniformity can be acquired by gas-phase coating, but available materials (e.g. parylene) don't have as high hydrophobicity as Teflon®. Self-assembly monolayer (SAM) may be a potential solution, but further investigation is obligatory to improve its hydrophobicity and durability in the methanol fuel of the actual working µDMFC system.

Table 1. Hydrophobic coating methods

	HMDS	Teflon®	parylene	SAM
Deposition environment	vapor	liquid	vapor	liquid
Danger of blocking the holes	no	yes	under control	no
Patterning	lift-off	RIE	RIE	lift-off
Equipment	simple	simple	specific coater	multi-step procedure
Hydrophobicity	relatively high	highest	relatively high	varies
Durability	short-term	long-term	long-term	can be long-term

Sub-micron breathing holes

Another important factor, which determines the feasibility of this breather, is the prevention of fuel leakage when the CO_2 gas bubbles are generated and breathed out, which increases the pressure inside the fuel chamber.

According to Laplace-Young's equation, $P_{inside} - P_{outside} \approx \frac{2s_f \cdot \sin q}{r}$, the maximum pressure difference that the breathing hole can withstand without leakage ($P_{inside} - P_{outside}$) is determined by the surface tension of the liquid s_f, the contact angle q, and the radius of the breathing holes r. This issue is vital for the actual methanol fuel cell because (1) both the surface tension and the contact angle of methanol solution are smaller than those of pure water, and (2) elevated working temperature (~80°C) further decreases surface tension. Under 1 atm pressurization, which is the usual pressure for the current prototype μDMFC with external pump, the maximum diameter of breathing holes, as limited by leakage prevention, can vary from 1.44μm (for pure water) to 0.34μm (for pure methanol), depending on the fuel concentration, which are beyond the usual photolithographic limitation of 2μm. Porous silicon etching, a promising technique to form submicron holes, is expected to improve the performance of our distributed breather for eventual integration in working μDMFC system.

CONCLUSION

The principle of distributed breathing is demonstrated by a breathing chip with 50μm-diameter Teflon®-coated hydrophobic breathing holes. Developing a series of techniques to fabricate stable, hydrophobic, submicron breathing holes is the focus of future work, aimed at integrating the distributed breather into a fully functional μDMFC system. The breather can also be fabricated and packaged into an individual device, so that it can be employed to collect gas bubbles and breathe them out from two-phase flows in many other degassing applications.

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